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Risø National Laboratory, DK-4000 Roskilde, Denmark
January 1988

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KINETICS AND MECHANISMS OF ELEMENTARY CHEMICAL PROCESSES OF IMPORTANCE IN COMBUSTION

Jette Munk, Palle Pagsberg, Emil Ratajczak,
Barbara Sztuba, and Alfred Sillesen

Abstract. The technique of pulse radiolysis combined with transient ultraviolet absorption spectrophotometry has been employed in spectrokinetic studies of shortlived free radical intermediates of importance in combustion. Various source reactions for vinyl, propargyl and carboxyl radicals have been investigated and the UV-spektre of these radicals have been recorded. The spectral features have been utilized in kinetic studies of the self-reactions of the radicals and the reactions with oxygen. Kinetic results on the reaction NO + NH_2 are also reported.

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KINETICS AND MECHANISM OF ELEMENTARY CHEMICAL PROCESSES OF IMPORTANCE IN COMBUSTION.
Spectrokinetic Studies of Vinyl Radicals.

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ENERGY CONSERVATION: COMBUSTION RESEARCH

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TABLE OF SYMBOLS

k_x Bimolecular rate constant in units of liter mol^{-1} s^{-1}

k^* Pseudo-first order rate constant, s^{-1}

ε Molar decadic extinction coefficient, liter mol^{-1} cm^{-1}

L Optical path length through the sample, cm

RESEARCH ACTIVITIES

Introduction.

Free radical mechanisms in the oxidation of hydrocarbons are of importance in combustion processes and in atmospheric chemistry. Detailed studies of reaction mechanisms and rates of elementary reactions can be achieved by a number of different experimental techniques which may differ with respect to the nature and the amount of information that can be gathered. The combination of pulse radiolysis and fast UV-spectrophometry employed at Risø National Laboratory allows the direct observation of transient species without interference from wall reactions and reaction rates can be studied in the temperature range of 300-400 K and at total pressures of 0.1 - 2.0 atm. In previous investigations we have recorded the ultraviolet spectra of selected alkyl and alkyl peroxy radicals and determined the absolute bimolecular rate constants for a number of elementary reactions. (1,2)
The rate of the reaction $R + O_2 + M \rightarrow RO_2 + M$ depends on the nature of the alkyl radical. In our previous work we have been concerned with $R = C_2H_5$ and $R = i\text{-}C_3H_7$ which may be classified as normal saturated alkyl radicals. The vinyl radical, $H\text{-}C{=}CH_2$ which is one on the simplest unsaturated radicals has been chosen as the subject of the present investigation and we present preliminary results on the spectral and kinetic features of vinyl radicals which could be obtained in high yields via suitable source reactions.

Experimental Section

The experimental setup for pulse radiolysis combined with tansient absorption spectrophotometry is shown in Figure 1.. Free radicals are produced by irradiation of a gas mixture with a 30-ns pulse of 2 MeV electrons from a Febetron 705 B field emission accelerator. A pulsed 150-W Xe lamp stabilized by optical feedback provides an analyzing light beam with very high intensity in the range of 200-500 nm. Via an optical system composed of Suprasil lenses, the analyzing light enters the sample cell where a set of internal aluminized mirrors provide optical pathlengths of 40,80 or 120 cm by multiple reflections. The spectral features are analysed using a 1-meter grating monochromator with a 1200 lines/mm grating which gives a reciprocal dispersion of 8 A/mm. The light intensity is monitored with a fast photomultiplier equipped with an S-20 cathode behind a Suprasil window. The output signals are digitized by a transient recorder and transferred to a PDP-11 minicomputer where the kinetic curves are filed together with specifications of the experimental conditions. The complete data files are finally transferred to a large central computer where the analysis of spectral and kinetic features takes place. Gas mixtures are prepared by admitting one component at a time to the sample cell and reading the corresponding partial pressure with a MKS Baratron Model 170 absolute electronic membrane manometer with a resolution of 10^{-5} bar. Electric heating and temperature control provide a range of sample temperatures from 298 to 400 K. A platinum resistance thermometer is used to measure the temperature of the gas mixture near the central part of the sample cell traversed by the analyzing light beam. The temperature variation is kept within ± 1 K. Computer modelling of chemical kinetics is used in the analysis of complex reaction mechanisms. We make use of a highly efficient computer program (R) which employs a fast semiinteractive procedure where calculated time profiles of selected species can be compared with stored experimental kinetic curves.

Results and discussion

Vinyl radicals were produced via the source reactions

(1) $H + C_2H_2 + M \rightarrow C_2H_3 + M$

(2) $Ar^* + C_2H_3Cl \rightarrow Ar + C_2H_3 + Cl$

(3) $Ar^* + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Ar + 2\ C_2H_3$

High yields of H-atoms were obtained by pulse radiolysis of H_2 and vinyl radicals were formed in the presence of small amounts of acetylen. The transient absorption signals were observed to build up with formation rates in accordance with (1) proceeding under pseudo-first order conditions, i.e. $\tau = \ln 2/k_1(C_2H_4)$. The absorption spectrum observed by radiolysis of 0.5% C_2H_2 in H_2 is shown in Fig.2. The yield of H-atoms in the radiolysis of H_2 was determined by the "titration reaction" $H + O_2 \rightarrow HO_2$ and using the well-known extinction coefficient of HO_2 we calculate $(H)_o = 2.80 \times 10^{-7}$ M. Likewise, at high concentrations of C_2H_2 all H-atoms are converted into vinyl radicals via (1). From the maximum of the absorption spectrum in Fig.2 which was recorded with an optical path length of 120 cm we calculate an extinction coefficient $\varepsilon(C_2H_3, 210nm) = 2000\ M^{-1}cm^{-1}$. The same absorption spectrum was observed by the Ar-sensitized reactions (2) and (3). In the radiolysis of Ar/1,3-C_4H_6 mixtures we observed the formation of vinyl radicals at the higher wavelengths as well as the consumption of 1,3-C_4H_6 at lower wavelengths where the parent molecule has a strong absorption band. In the overlap region we found an isosbestic point at 220 nm as shown in Fig.3. At this wavelength $\varepsilon(C_2H_3) = \varepsilon(1,3\text{-}C_4H_6)/2 = 1825\ M^{-1}cm^{-1}$ which is in good agreement with the value based on the yield of H-atoms. Thus, the spectral assignment seems well established and the strong ultraviolet absorption band may be used in studies of the fate of vinyl radicals in different chemical environments.

Kinetics of the C_2H_3 self-reaction.

The self reaction of vinyl radicals involves the combination and disproportionation reactions (4a) and (4b)

(4a) $2\ C_2H_3\ (+\ M) \rightarrow 1,3\text{-}C_4H_6\ (+\ M)$

(4b) $2\ C_2H_3 \rightarrow C_2H_2 + C_2H_4$.

The decay curves shown in Fig.4 cannot be accounted for by the self reaction alone because of the high tail-ends which seem to indicate the build-up of a very long-lived or stable species. We suspect that vinyl radicals may add to the double bonds in the parent compounds to form polymer radicals which may also absorb light in the same spectral region. To overcome these difficulties we have considered other source reactions for C_2H_3, and recently we have successfully applied RH + F -> R + HF as a source of CH_3, C_2H_5, CH_2OH and other radical species. Therefore we may expect that high yields of vinyl radicals can be obtained in the reaction

(5) $C_2H_4 + F \rightarrow C_2H_3 + HF$

The combination of F-atoms is fairly slow and we expect that nearly 100% conversion via (5) can be obtained using only a moderate excess of ethylen, e.g. $(C_2H_4)_o = 2x(F)_o$. Under such experimental conditions the formation of polymer radicals may be avoided and the decay rate should be controlled by the self reaction, (4a) and (4b).

Discussion

The ultraviolet absorption spectrum of the vinyl radical is much stronger than the visible band reported previously (3) and our preliminary work suggests that the 210 nm band may be useful in kinetic studies. In addition to the self reaction we want to study the reaction $C_2H_3 + O_2$ -> products.

Future work

We want to investigate the reactions RH + F -> R + HF which may be used to produce various alkenyl radicals under experimental conditions where the self reactions and the reactions with oxygen can be studied without interference from competing reactions. The radicals C_2H, C_2H_3 and C_3H_3 are of particular interest in combustion and soot formation processes.
In addition to the unsaturated radicals there is a need to study various oxygen containing radicals which may also be produced by H-abstraction from alcohols, ketones and carboxylic acids using F-atoms which can be obtained in high yields by pulse radiolysis of Ar/SF_6 og Ar/F_2 mixtures. Most of these radicals are expected to absorb light in the region 200-350 nm and the kinetics may be studied by transient spectrophotometry.

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(1) Spectrokinetic Studies of Ethyl and Ethylperoxy Radicals
Jette Munk, P. Pagsberg, E. Ratajczak and A. Sillesen.
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Jette Munk, P. Pagsberg, E. Ratajczak and A. Sillesen.
Submitted to Chem. Phys. Letters.

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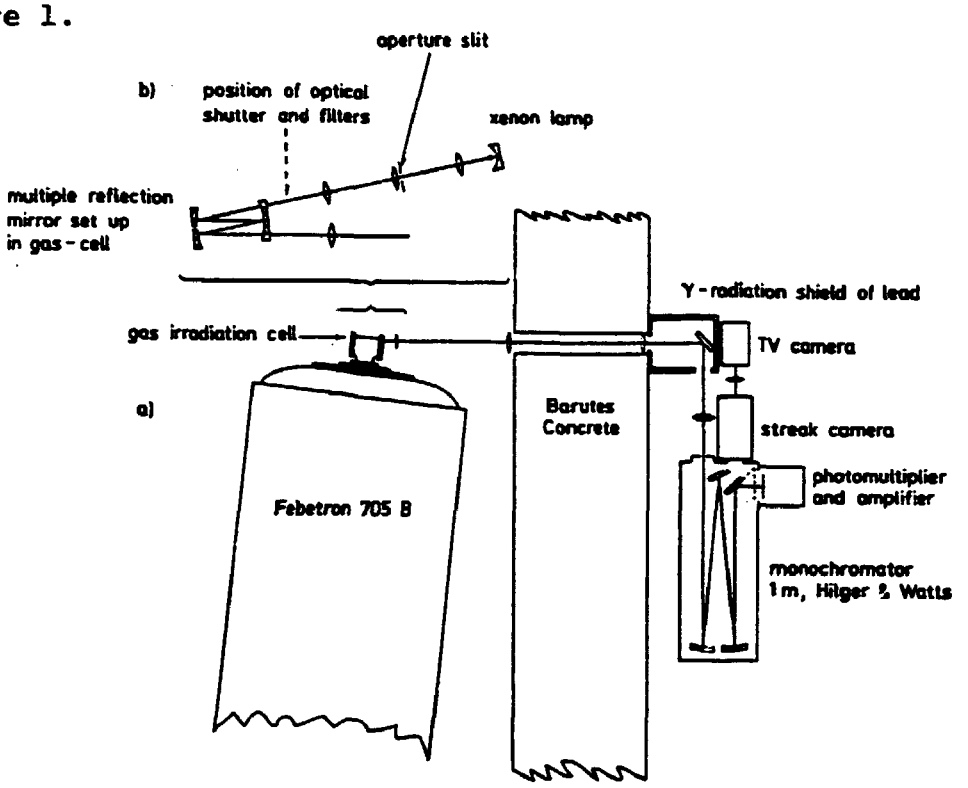
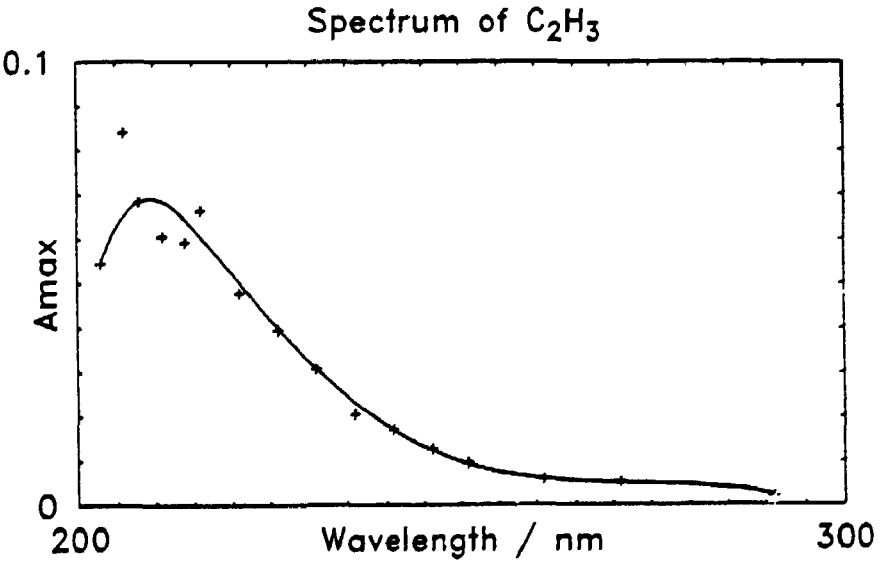
Figure 1.



Experimental set-up for pulse radiolysis combined with transient ultraviolet spectrophometry.
RISØ National Laboratory, Roskilde, Denmark.



Isosbestic point at 221 nm; $2\varepsilon(C_2H_3)=\varepsilon(1,3-C_4H_6)$

$Ar^* + 1,3-C_4H_6 \rightarrow Ar + 2\ C_2H_3$

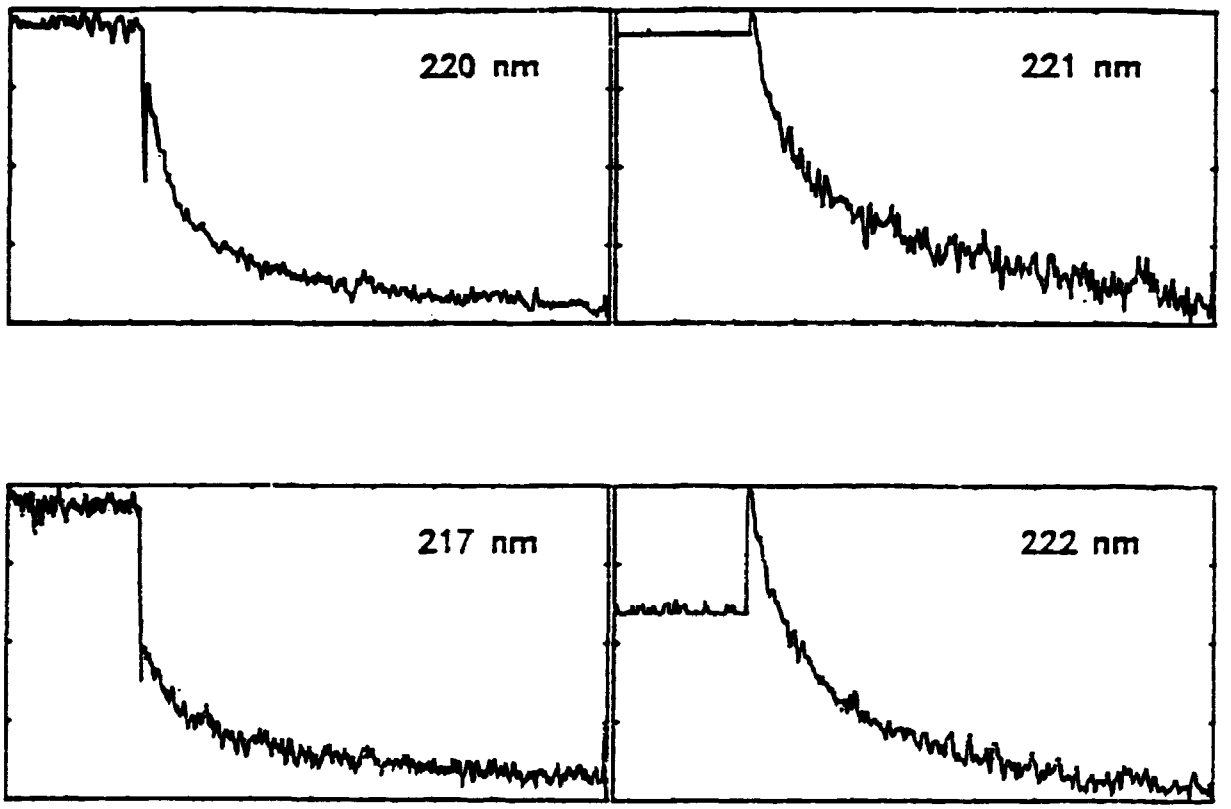
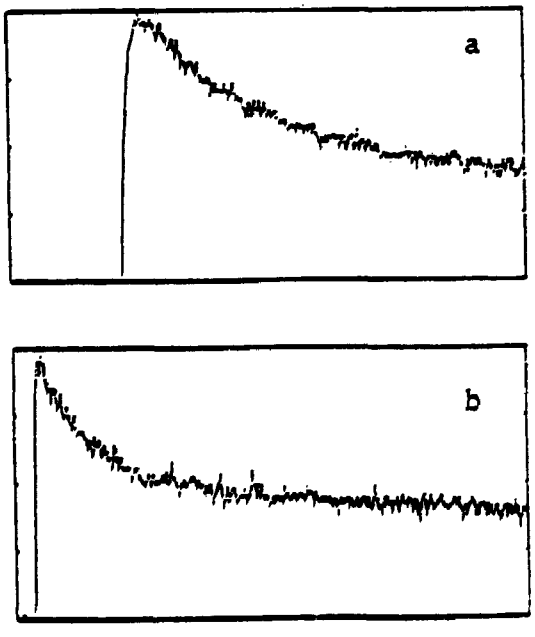


Figure 4.



Decay of vinyl radicals produced via different source reactions.

(a) Ar-sensitized dissociation of C_4H_6. Pulse radiolysis of 0.1% 1,3-C_4H_6 in Ar at 1 atm and T=295 K. 240 nm. 200 us

(b) Ar-sensitized dissociation of C_2H_3Cl Pulse radiolysis of 0.4% C_2H_3Cl in Ar. 240 nm. A_{max} = 0.220. Time scale 400 us

KINETICS AND MECHANISM OF ELEMENTARY CHEMICAL PROCESSES OF IMPORTANCE IN COMBUSTION

Spectrokinetic Studies of Vinyl and Propargyl Radicals.

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(3) SUMMARY

In the present report we present new experimental results obtained in our spectrokinetic studies of alkenyl radicals. In our spectrokinetic studies of vinyl radicals we have employed the following source reactions:

(1) $H + C_2H_2 + M \rightarrow C_2H_3 + M$

(2) $Ar^* + C_2H_3Cl \rightarrow Ar + C_2H_3 + Cl$

(3) $Ar^* + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Ar + 2\ C_2H_3$

(4) $Ar^* + CH_2{=}CH{-}CH_3 \rightarrow Ar + C_2H_3 + CH_3$

(5) $F + C_2H_4 \rightarrow HF + C_2H_3$

These reactions were initiated by pulse radiolysis of gas mixtures containing low partial pressures of the parent compounds backed up with H_2 or Ar to a pressure of 1 atm. The vinyl radical has a broad absorption band with a maximum at 215 nm. The kinetic features were studied by monitoring the transient absorption signals at 215 nm or other suitable wavelengths within the absorption band.
The reaction of vinyl radicals with oxygen is of particular interest in combustion chemistry and the following reaction path ways have been considered:

(6a) $C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$

(6b) $M + C_2H_3 + O_2 \rightarrow C_2H_3O_2 + M$

(6c) $C_2H_3 + O_2 \rightarrow CH_2O + CHO$

In the presence of oxygen we have observed the replacement of the vinyl radical by a longlived transient species with an absorption spectrum which is different from those of HO_2 and CHO. Based on these observations we conclude that reaction (6b) is the main channel at T = 298 K and p = 1 atm.
We also report some preliminary experimental results on the propargyl radical produced via the source reaction:

(9) $Ar^* + C_3H_3Br \rightarrow Ar + C_3H_3 + Br$

The subsequent combination of Br-atoms was followed by monitoring the build-up of Br_2 at 400 nm. The ultraviolet band of C_3H_3 with a maximum at 250 nm which we observed in the present investigation has not been reported previously.
In order to prove the assignment we want to try other source reactions for the propargyl radical. Subsequently we want to study the reaction $C_3H_3 + O_2 \rightarrow$ products.

(4) OBJECTIVE

Alkenyl Radicals is an important class of intermediate species in combustion processes. While a lot of information is available on the spectral and kinetic features of saturated alkyl radicals i.e. CH_3, C_2H_5, C_3H_7 etc. there is a lack of knowledge on spectra and kinetics of unsaturated radicals. The unsaturated hydrocarbon radicals are thought to play an important role in soot formation and most likely also in the formation of aromatic products.

The objective of our current experimental work is to provide the necessary information on the UV-spectra of simple unsaturated hydrocarbon radicals, such as ethynyl (C_2H), vinyl (C_2H_3) and propargyl (C_3H_3).
Once the spectra have been recorded the kinetics of the various radicals may be studied directly in different chemical environments by monitoring the transient absorption signals corresponding to the particular UV-band. Of particular interest is the mechanism and rate of the self reaction of each individual alkenyl radical as well as the reaction with molecular oxygen.
The expected differences in the structure and reactivity of the isomeric C_3H_3 radicals may eventually be verified by spectrokinetic studies provided that the absorption spectra can be distinguished. Two of the isomers may be represented by the propargyl-propadienyl electronic resonance-hybrid, i.e. $HC{=}C{=}CH_2 \leftrightarrow HC{\equiv}C{-}CH_2$. Trimethine is a structural isomer which is also resonance stabilized, $\cdot CH{=}CH{-}CH: \leftrightarrow :CH{-}CH{=}CH\cdot$, i.e. a carbene-radical. The trimethine radical may dimerize to form benzene, $2\ C_3H_3 \rightarrow C_6H_6$. The different structural isomers may eventually be obtained from different parent compounds, e.g. propargyl bromide and allene.

(5) INTRODUCTION

Pulse radiolysis appears to be a very versatile technique for the production of various types of hydrocarbon radicals. High yields of H-atoms are obtained in the radiolysis of H_2 and in the presence of unsaturated hydrocarbon molecules alkyl or alkenyl radicals may be formed,

(a)	$H + C_2H_4 + M \rightarrow C_2H_5 + M$	(ethyl)
(b)	$H + C_2H_2 + M \rightarrow C_2H_3 + M$	(vinyl)

F-atoms are produced by the Ar-sensitized radiolysis of SF_6 and subsequently the F-atoms may abstract H-atoms, e.g.

(c)	$F + C_2H_6 \rightarrow HF + C_2H_5$	(ethyl)
(d)	$F + C_2H_4 \rightarrow HF + C_2H_3$	(vinyl)

The direct Ar-sensitized radiolysis of hydrocarbon molecules may also be used as source reactions for free radicals, e.g.

(e)	$Ar^* + CH_3COCH_3 \rightarrow Ar + CO + 2\ CH_3$	(methyl)
(f)	$Ar^* + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Ar + 2\ C_2H_3$	(vinyl)

Alkyl or alkenyl halides may also be used as parent compounds

(g)	$Ar^* + CH_3I \rightarrow Ar + CH_3 + I$	(methyl)
(h)	$Ar^* + C_2H_3Cl \rightarrow Ar + C_2H_3 + Cl$	(vinyl)

The use of different types of source reactions for the same radical is important in verifying the spectral assignment for transient species which have not been observed before. In the case of vinyl we have observed the same UV-spectrum using different source reactions. Thus, the assignment of the transient absorption to C_2H_3 may be taken with confidence. The concentration time profiles of vinyl radicals may now be recorded in different chemical environments by monitoring the transient absorption signals. Rate constants for different elementary reactions such as radical self reactions or reactions with molecular oxygen can be evaluated from the absorption time profiles.

(6) CONCLUSIONS

The combustion of hydrocarbon fuels is governed by two main path ways, i.e. pyrolysis and oxidation via free radicals. Large hydrocarbon molecules and polyatomic radicals degrade by pyrolysis into smaller fragments which are more stable towards thermal decomposition, i.e. the lower alkenes and alkynes e.g. C_2H_4 and C_2H_2 as well as the alkyl radicals CH_3 and C_2H_5 and the unsaturated carbon-rich radical species C_2H, C_2H_3 and C_3H_3.
The oxidation of the lower alkyl radicals has been studied in great detail but virtually nothing is known about the fate of the unsaturated radicals. Thus, in the case of vinyl radicals it has been presumed that the high temperature reaction is analogous to that of alkyl radicals, i.e. H-atom transfer

(6a) $C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$ $\Delta H = -10$ kcal/mol

In the present investigation we have recorded a hitherto unknown UV-band of C_2H_3 which can be used for direct kinetic studies of the vinyl radical in different chemical environments. In one series of experiments we have studied the fate of vinyl radicals produced via reaction (1) initiated by pulse radiolysis of $C_2H_2/O_2/H_2/Ar$ mixtures. In the presence of small amounts of oxygen we have observed the build-up of strong transient absorption signals at 230 nm which cannot be accounted for by HO_2 produced via reaction (6a) because the estimated value of the extinction coefficient of the transient species $\varepsilon(X) >> \varepsilon(HO_2)$ at 230 nm. In addition, the life time of the transient species is much longer than that of HO_2 decaying via the self reaction:

(7) $HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$

To explain the experimental results we have considered two other exothermic reaction channels:

(6b) $M + C_2H_3 + O_2 \rightarrow C_2H_3O_2 + M$ $\Delta H = -30$ kcal/mol

(6c) $C_2H_3 + O_2 \rightarrow HCO + H_2CO$ $\Delta H = -86$ kcal/mol

Under the experimental conditions employed the formyl radicals produced in reaction (6c) would be rapidly converted into HO_2:

(8) $HCO + O_2 \rightarrow CO + HO_2$

Since HO_2 would be the common product of (6a) and (6c) + (8) we conclude that reaction (6b) must be the most important channel at T = 298 K and p = 1 atm. Thus, we assign the longlived component of the transient absorption signals to the vinylperoxy radical formed via reaction (6b). From the observed rate of formation monitored at 230 nm we have calculated $k_{6b} = 1.3 \times 10^9$ $M^{-1}s^{-1}$. Similar experiments have been caried out using the source reactions (2) and (3) and monitoring the build-up of $C_2H_3O_2$ at 277 nm where overlap with the absorption spectra of HO_2 and HCO is negligible.
A value of $k_{6b} = (1.5 \pm 0.5) \times 10^9$ $M^{-1}s^{-1}$ has been obtained as an average of three independent series employing different source reactions, i.e. (1), (2) and (3).

Having discovered the strong UV-band of C_2H_3 we assumed that also the propargyl radical might have a characteristic band that could be used for kinetic studies. The Ar-sensitized radiolysis of propargyl bromide was investigated and we observed a strong absorption band with a maximum at 250 nm which we assigned to C_3H_3. Transient absorption signals were also observed at the 0-0 band of the $^2B_1$-$^2B_1$ transition of C_3H_3 at 332 nm (ref. 1). The simultaneous formation of Br-atoms via the source reaction $Ar^* + C_3H_3Br \rightarrow Ar + C_3H_3 + Br$ was verified by monitoring the build-up of Br_2 absorption at 400 nm. Knowing the UV-absorption spectrum of C_3H_3 we may now study the self-reaction of propargyl radicals as well as the reaction with molecular oxygen.

(7) TABLE OF SYMBOLS

k_x Bimolecular rate constant in units of liter/mol sec

k^* Pseudo-first order rate constant, sec^{-1}

ϵ Molar decadic extinction coefficient, liter/mol cm

L Optical path length through the sample, cm

(8) EXPERIMENTAL

Unsaturated hydrocarbon radicals were produced by pulse radiolysis of gas mixtures containing suitable parent compounds. In a typical experiment the gas mixture was irradiated with a 30 ns pulse of 2 MeV electrons and the yields of the primary radicals were in the order of 10^{-6} mol/liter. The radicals were detected by UV-spectrophotometry employing a 150 W pulsed high pressure Xe-lamp stabilized with optical feed-back as the analyzing light source and a 1 meter grating monochromator with a 1200 lines/mm grating transmitting a band pass of 8 Å per mm slit width. Under these conditions the transient absorption signals characteristic to the free radicals could be recorded with a good signal-to-noise ratio.

Vinyl Radicals.
The UV-spectrum presented in our first report was used in studies of the reaction of vinyl radicals with molecular oxygen. Typical gas mixtures contained $C_2H_2/H_2/Ar$, C_2H_3Cl/Ar and $1,3\text{-}C_4H_6/Ar$ as the major components and increasing amounts of O_2 was added to study the change in kinetics.

Propargyl radicals.
The Ar-sensitized decomposition of propargyl bromide was used as a source reaction. Typical gas mixtures containing 1 mbar of C_3H_3Br in 1 atm Ar were irradiated and strong absorption signals were observed in the range of 230-332 nm.

(9) RESULTS AND DISCUSSION

Spectrokinetic Studies of Vinyl Radicals

The mechanism and kinetics of the reaction of vinyl radicals with molecular oxygen is of interest in combustion chemistry. So far it has been presumed that the reaction at high temperatures is analogous to the reaction between saturated alkyl radicals and oxygen, i.e. H-atom transfer:

(6a) $C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$

Knowing the spectra of C_2H_3 and HO_2 this assumption may be tested by monitoring the kinetics at different wave lengths. The observation of the build-up of strong transient absorption signals at 230 nm could not be accounted for by HO_2 produced in reaction (6a). Other reaction channels give rise to the formation of vinylperoxy or formyl radicals via

(6b) $M + C_2H_3 + O_2 \rightarrow C_2H_3O_2 + M$

(6c) $C_2H_3 + O_2 \rightarrow HCO + H_2CO$

The experimental evidence is in favour of reaction (6b) and from the observed formation kinetics of $C_2H_3O_2$ we have determined the rate constant under different experimental conditions as shown in the table below.

Chemical composition	Wavelength nm	k(6b) $M^{-1}s^{-1}$
$C_2H_2/O_2/H_2/Ar$	230	1.3×10^9
$C_2H_3Cl/O_2/Ar$	277	1.6×10^9
$1,3\text{-}C_4H_6/O_2/Ar$	277	1.7×10^9

$$k(6b)_{av} = (1.5 \pm 0.2) \times 10^9 \ M^{-1}s^{-1}$$

The reaction between vinyl radicals and molecular oxygen has also been studied (ref.2) by laser flash photolysis combined with photoionization mass spectrometry. In the pressure range of 1-4 mbar reaction (6c) was found to be the predominant channel with a rate constant of 6.1×10^9 $M^{-1}s^{-1}$ at 298 K. The reaction is thought to proceed via an short lived adduct decomposing into the smaller fragments via a cyclic transition state. Under the experimental conditions employed in the present investigation it appears that the adduct is stabilized by collisional deactivation making reaction (6b) the most important channel at a pressure of 1 atm.

Spectrokinetic Studies of Propargyl Radicals

In our preliminary studies of propargyl radicals we have observed an ultraviolet absorption band which has not been reported previously. The spectrum shown in Fig.1 was obtained from the maxima of the transient absorption signals of C_3H_3 produced by the Ar-sensitized radiolysis of propargyl bromide:

(P1) $Ar^* + C_3H_3Br \rightarrow Ar + C_3H_3 + Br$

The release of Br-atoms in reaction (P1) was verified by observing the build-up of Br_2 monitored at 400 nm. In addition to the strong band at 250 nm we also observed transient absorption signals at the 0-0 band of the weak $\pi - \pi$ $^2B_1$-$^2B_1$ transition which is located at 332 nm. (ref.1)

The decay of C_3H_3 monitored at 332 nm is shown in Fig.2. The shape of the decay curve is in accordance with simple second order kinetics. The self-reaction (P2) proceeds in competition with the recombination reaction (P3):

(P2) $2\ C_3H_3 \rightarrow$ products

(P3) $C_3H_3 + Br \rightarrow C_3H_3Br$

(P4) $M + Br + Br \rightarrow Br_2 + M$

The yield of Br_2 via (P4) was used to estimate a lower limit of the C_3H_3 yield in reaction (P1).

(11) Future Work

In the present report we have presented the strong UV-spectrum of the propargyl radical which may be used in kinetic studies. The reaction of propargyl radicals with molecular oxygen is of particular interest because of the possibility of different product channels. If the propargylperoxy radical is formed we may expect a weak $R-O_2$ bond due to resonance stabilization of the propargyl radical. Thus, a thermal equilibrium may be studied even at moderately low temperatures. This would allow us to determine ΔH and ΔS for the reaction as well as the bond energy, $D(R-O_2)$.

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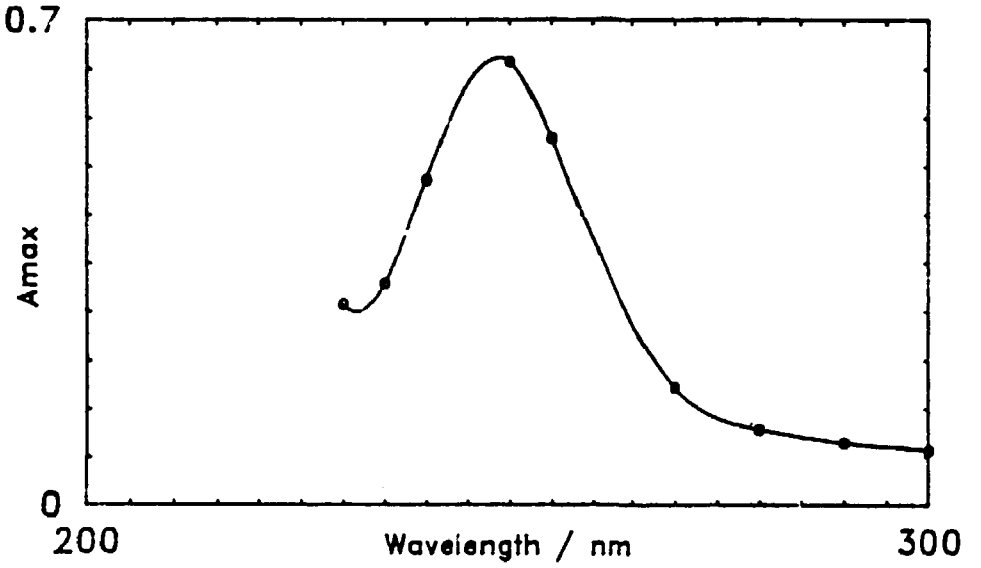
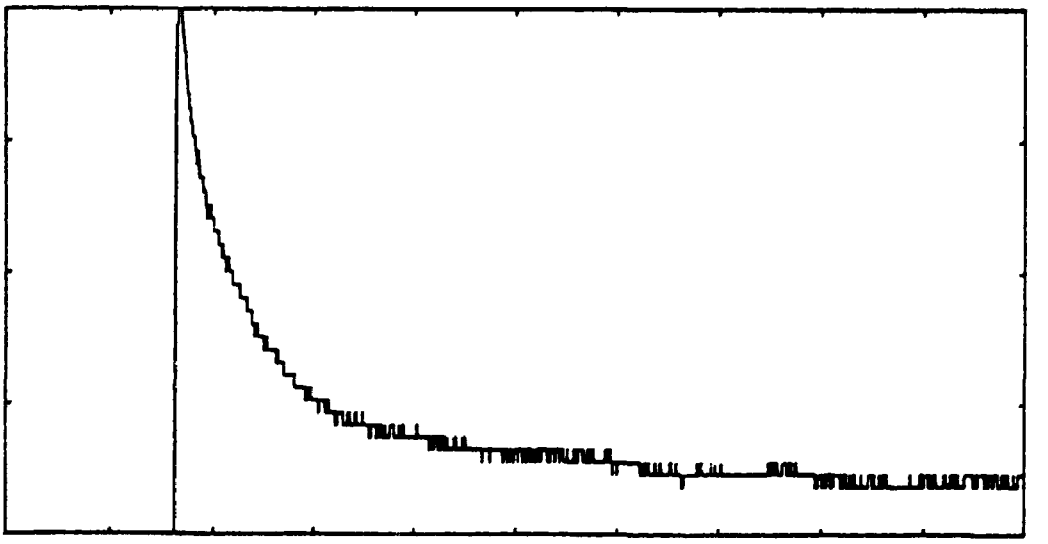
SPECTRUM AND KINETICS OF PROPARGYL RADICALS

Spectrum of C_3H_3 radical



Source reaction: Ar* + C_3H_3Br -> Ar + C_3H_3 + Br;
Strong absorption by the parent compound at wavelengths below 230 nm.

C_3H_3 radical decay monitored at 332 nm



A_{max} = 0.088 t_{max} = 400 μs

Source reaction: (P1) Ar* + C_3H_3Br -> Ar + C_3H_3 + Br

Competing reactions: (P2) 2 C_3H_3 -> products

(P3) C_3H_3 + Br -> C_2H_3Br

EN3E-095-DK (B)
April 1987

KINETICS AND MECHANISM OF ELEMENTARY CHEMICAL REACTIONS OF IMPORTANCE IN COMBUSTION

Spectrokinetic Studies of Propargyl Radicals

Kinetics of the reaction NH_2 + NO

UV-spectrum of COOH/HCOO

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ENERGY CONSERVATION: COMBUSTION RESEARCH

October 1987

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(3) SUMMARY

The rate of the reaction of propargyl radicals with oxygen has been studied by pulse radiolysis of Ar/C_3H_3Br/O2 mixtures. Propargyl radicals were formed in the Ar-sensitized radiolysis of propargyl bromide and transient absorption signals due to C_3H_3 were monitored at 332 nm. In the absence of oxygen the decay rate is governed mainly by the self reaction of C_3H_3 with a small contribution from the C_3H_3 + Br cross reaction. In the presence of oxygen the decay rate was found to increase in accordance with the reaction C_3H_3 + O2 -> products, and the rate constant for this reaction was determined from a plot of reciprocal half-lives versus oxygen concentration.
We have also explored a number of radical source reactions based on the Ar-sensitized radiolysis of SF_6,

(I) $Ar^* + SF_6 \rightarrow Ar + SF_5 + F$

(II) $F + RH \rightarrow HF + R$

using RH = CH_4, H_2O, NH_3, and HCOOH. The initial yield of F-atoms was determined by monitoring the transient absorption of CH_3 produced by radiolysis of Ar/SF_6/CH_4 mixtures. The observed decay of CH_3 was found to be in good agrement with recommended values of $2k(CH_3)$ and $\varepsilon(CH_3)$.
Similar experiments were carried out with RH = H_2O and NH_3 and the the transient absorption signals of OH and NH_2 were monitored at 309.0 nm and 597.6 nm, respectively. We have measured the overall decay rate of NH2 in the presence of NO and simultaneously we have tried to determine the yield of OH and the branching ratio for the two product channels, i.e. $NH_2 + NO \rightarrow N_2 + H_2O$ and $NH_2 + NO \rightarrow N_2H + OH$.
Reaction (II) was also used with RH = HCOOH and the observed transient absorption signals in the range of 216-300 nm may be assigned to COOH and/or HCOO radicals.
Preliminary kinetic results have been obtained with a new experimental set-up based on pulse radiolysis combined with IR-diodelaser spectrophotometry.

(4) OBJECTIVE

The objective of our experimental work is to study the chemical reactivity of free radicals in combustion.
High yields of free radicals are produced by pulse radiolysis of suitable gas mixtures and the electronic absorption spectra and concentration versus time profiles of the transient species are recorded by time resolved spectrophotometry in the 200-800 nm region. Using this technique it is possible to study the rate and mechanism of chemical elementary reactions, e.g. reactions of various alkyl radicals with oxygen.
While a lot of kinetic information is available on simple alkyl radicals there is a lack of knowledge on the chemical reactivity of the unsaturated radicals. We have explored a number of source reactions for vinyl and propargyl radicals and recorded the UV-spectra of these transient species. We are now studying the rate and mechanism of the reactions of C_2H_3 and C_3H_3 with O_2.
In addition to alkoxy and alkyl peroxy radicals there are other oxygen containing radicals which are important in combustion. We have tried to find suitable source reactions for such radicals and in the present report we present some preliminary results on COOH radicals.
The development of methods to reduce NO_x emissions from flue gas is an important task in combustion research. The reaction NH_2 + NO has been studied by different experimental techniques to establish the overall rate and the branching into various product channels. We have studied the reaction and tried to measure the relative yield of hydroxyl radicals produced in the reaction NH_2 + NO -> N_2H + OH which may be an important product channel, at least at high temperatures.

(5) INTRODUCTION

Alkenyl Radicals are thought to play an important role in the formation of soot and aromatic combustion products. However, alkenyl radicals may also react with oxygen to form other products like carbonyl compounds which may undergo further oxidation into CO or CO_2.

In the previous report we presented our kinetic results on the reaction of vinyl radicals with oxygen. We have now studied the reaction of propargyl radicals with oxygen at atmospheric pressure. The rate constant obtained in the present study is compared with the results of recent low pressure studies by I. Slagle and D. Gutman.

Along with our kinetic studies of alkyl and alkenyl radicals we have also investigated a number of NO_x reactions including NO_3 reactions of relavance to atmospheric chemistry.

The mechanism of the reaction NH_2 + NO has been the subject of numerous investigations. However, in view of unsettled question regarding the relative importance of various product channels we have made an attempt to mesure the yield of OH produced in the reaction NH_2 + NO -> N_2H + OH which may play an important role, in particular at high temperatures.

The reaction HO + CO -> H + CO_2 is the most important source of CO_2 in the combustion of coal and hydrocarbons. The reaction proceeds via an adduct HOCO which may be stabilized under certain experimental conditions. We have investigated the reaction F + HCOOH which may give rise to two isomeric radicals, i.e. COOH and HCOO. In our preliminary studies we have observed transient absorption signals in the range of 210-300 nm which may be assigned to COOH and/or HCOO.

(6) CONCLUSIONS

We have studied the reaction of propargyl radicals with molecular oxygen at T = 298 K and p = 1 atm.
The mechanism appears to be a simple addition reaction with a fairly low rate constant, $k = (1.0 \pm 0.2) \times 10^8\ M^{-1}s^{-1}$.

In studies of the reaction NH_2 + NO we have measured the overall rate constant, $k = (1.3 \pm 0.3) \times 10^{10}\ M^{-1}s^{-1}$. In addition we have estimated an upper limit for the branching ratio of the reactions
(1) $NH_2 + NO \rightarrow N_2H + OH$ and (2) $NH_2 + NO \rightarrow N_2 + H_2O$,
i.e. $k_1/(k_1 + K_2) < 0.08$.

The reaction of P-atoms with formic acid has was used to produce transient species absorbing in the range of 220-300 nm.
The UV-spectrum may be assigned to COOH and/or HCOO.

(7) TABLE OF SYMBOLS

k_x Bimolecular rate constant in units of liter/mol sec

k^* Pseudo-first order rate constant, sec^{-1}

ε Molar decadic extinction coefficient, liter/mol cm

L Optical path length through the sample, cm

(8) EXPERIMENTAL

High yields of free radicals were obtained by pulse radiolysis of gas mixtures containing suitable parent compounds.
In a typical experiment the gas mixture was irradiated with a 30 ns pulse of 2 MeV electrons and the yield of the primary radicals were in the order of 10^{-6} mol/l. The radicals were monitored by UV-spectrophotometry employing a 150 W high pressure Xe-lamp as the analyzing light source. By pulsing the Xe-lamp we obtain a fifty fold increase in the brightness which improves the signal-to noise ratio in the UV-region. In pulsed operation the output from the lamp is stabilized by optical feed-back to obtain a constant light intensity during 0-50 msec. The analyzing light beam is passed through the sample with internal mirrors providing an optical path length of 40, 80 or 120 cm. The transient absorption signals are monitored using a fast photomultiplier at the exit slit of a 1 meter grating monochromator with a 1200 lines/mm grating transmitting a band pass of 8 Å per mm slit width.

Propargyl Radicals

The Ar-sensitized decomposition of propargyl bromide was used to obtain high yields of C_3H_3. Typical gas mixtures containing 1 mbar of C_3H_3Br in 1 atm Ar were irradiated and strong absorption signals were observed in the range of 230 - 332 nm.

OH, NH_2 and COOH/HCOO Radicals

High radical yields were obtained via the reactions
$Ar^* + SF_6 \rightarrow Ar + SF_5 + F$; and $F + RH \rightarrow HF + R$;
which were initiated by pulse radiolysis of $Ar/SF_6/RH$ mixtures where RH = H_2O, NH_3 or HCOOH.

(9) RESULTS AND DISCUSSION

Kinetics of the Reaction of Propargyl Radicals with Oxygen

The mechanism of the reaction of C_3H_3 with O_2 has recently been investigated by Slagle and Gutman (1) employing a tubular reactor coupled to a photoionization mass spectrometer. The reaction was studied at low pressures and over a temperature range of 293-865 K. At low temperatures a simple reversible addition was observed, and the equilibrium constant for $C_3H_3 + O_2 = CH_2O_2$ was measured as a function of temperature. The observed rate constant for the forward reaction was found to be pressure dependent and apparently in the middle of the falloff region in the applied pressure range of 0.8-2.5 mbar. In the present investigation we have studied the rate of the addition reaction at p = 1 atm to provide more information on the shape of the fall-off curve. The following reactions account for the observed kinetics of C_3H_3 monitored at 332 nm with an optical path length of 120 cm and a spectral band pass of 0.2 nm.

(1) $Ar^* + C_3H_3Br \rightarrow Ar + C_3H_3 + Br$

(2) $2\ C_3H_3 + M \rightarrow$ products

(3) $C_3H_3 + Br + M \rightarrow C_3H_3Br + M$

(4) $2\ Br + M \rightarrow Br_2 + M$

(5) $C_3H_3 + O_2 + M \rightarrow C_3H_3O_2 + M$

(6) $C_3H_3O_2 + M \rightarrow C_3H_3 + O_2 + M$

In the absence of oxygen we observed simple second order kinetics in accordance with the self-reaction (2). High yields of Br_2 were monitored at 400 nm indicating that $k_3 << k_2$. In the presence of oxygen we observed simple exponential decay curves, and the rate constant for reaction (5) was derived from a plot of reciprocal half-lives versus $p(O_2)$ as shown in Fig.1.

The value of the apparent bimolecular rate constant obtained in the present study $k_5 = (1.0 \pm 0.2) \times 10^8$ $M^{-1}s^{-1}$ at T = 298 K and p = 1 atm may be compared with the value of Slagle and Gutman (1) $k_5 = 2.7 \times 10^7$ $M^{-1}s^{-1}$ at T = 293 K and p = 1.86 torr. The relatively low value obtained at 1 atm would seem to indicate that experiments at higher pressures are required in order to establish the true high pressure value of k_5. Work is in progress to calculate the high pressure limit and the shape of the fall-off curve using the method developed by Troe and co-workers. (2)

Rate and mechanism of the reaction NH_2 + NO

at T = 298 K and p = 1 atm.

We have re-investigated this important reaction by monitoring the transient absorption signals of NH_2 and OH at 597.6 nm and 309.0 nm, respectively. The Ar-sensitized radiolysis of SF_6 was employed to obtain a high yield of F-atoms which were consumed in the subsequent H-abstraction reactions:

(1) $F + NH_3 \rightarrow HF + NH_2$

(2) $F + H_2O \rightarrow HF + OH$

These reactions were initiated by pulse radiolysis of mixtures containing 2-5 mbar NH_3 or H_2O and 50 mbar SF_6 backed up with Ar to 1 atm at T = 298 K. Reaction (2) was used as a reference to calibrate the transient absorption signals of OH under experimental conditions where all F-atoms are consumed in (2), i.e. $(OH)_{max} = (F)_o$.

The decay of NH_2 observed by pulse radiolysis of $Ar/SF_6/NH_3$ was simple second order in accordance with the self-reaction:

(3) $2\ NH_3 + M \rightarrow N_2H_4 + M$

Combining the initial yield $(NH_2)_{max} = (F)_o$ with the observed decay half-life we obtain $2k_3 = 5.1 \times 10^{10}$ $M^{-1}s^{-1}$ which is in good agreement with our previous studies at T = 298 K and with $p(M) = p(NH_3) = 1$ atm. (3)

From the increase in the decay rate in the presence of NO we have derived a value of the overall rate constant k_4 for the sum of the proposed reactions:

(4a) $NH_2 + NO = (NH_2NO)^*$

(4b) $(NH_2NO)^* \rightarrow N_2 + H_2O$

(4c) $(NH_2NO)^* \rightarrow N_2H + OH$

(4d) $(NH_2NO)^* + M \rightarrow NH_2NO + M$

The value of $k_4 = 1.3 \times 10^{10}\ M^{-1}s^{-1}$ was obtained from the slope of reciprocal half-lives versus p(NO) shown in Fig.2. The value obtained in the present study is in good agreement with the results of previous investigations. (4,5)
Attempts to measure the yield of OH produced via reaction (4c) were not successful. Based on the signal-to-noise ratio of the transient OH absorption signals obtained with $Ar/SF_6/H_2O$ we estimate a detection limit of $\delta(OH) = 0.05(F)_o$, i.e. we might expect to observe OH signals if (4c) amounts to 5% of the overall reaction. We have estimated an upper limit of 8 % for the relative yield of reaction (4c). This value is based on computer simulations of the reactions (1),(3) and (4) taking into account the losses of OH via the reactions (2),(5) and (6).

(5) $OH + NH_3 \rightarrow H_2O + NH_2$

(6) $OH + NO + M \rightarrow HONO + M$

Thus, it appears that reaction (4c) is rather unimportant at room temperature and atmospheric pressure. Under these experimental conditions the adduct may eventually be collision stabilized via reaction (4d). However, the stability of NH_2NO is expected to be low and thermal as well as surface catalyzed decomposition may take place even at room temperature.

UV-spectrum of COOH/HCOO

The two isomeric radicals COOH and COOH may be produced by abstraction of H-atoms from formic acid. By abstraction with F-atoms one might expect a branching ratio of $k_1/(k_1+k_2) = 0.5$ in view of the high H-F bond energy.

(1) $F + HCOOH \rightarrow HF + COOH$

(2) $F + HCOOH \rightarrow HF + HCOO$

The spectrum of the transient species produced by radiolysis of $Ar/SF_6/HCOOH$ mixtures is shown in Fig.3.

The observed second order decay indicate radical combination and/or disproportionation reactions, e.g.

(3) $2\ COOH \rightarrow (COOH)_2$

(4) $2\ COOH \rightarrow HCOOH + CO_2$

(5) $2\ HCOO \rightarrow HCOOH + CO_2$

So far we have no direct evidence for the presence of two different transient species, i.e. COOH and HCOO and it may be difficult to distinguish between the two radicals based on kinetic observations.

I order to identify the aborbing species we may try other source reactions, e.g.

(6) $HO + CO + M \rightarrow COOH + M$

(7) $H + CO_2 + M \rightarrow COOH/HCOO + M$

(8) $Ar^* + HCOOCH_3 \rightarrow Ar + HCOO + CH_3$

In general the carboxyl radicals R-COO may be obtained by the Ar-sensitized radiolysis of various esters, i.e.

(9) $Ar^* + R_1COOR_2 \rightarrow Ar + R_1COO + R_2$

(10) $Ar^* + R_1COOR_2 \rightarrow Ar + R_1 + COOR_2$

Using $R_1 = CH_3$ and $R_2 = CD_3$ it may be possible to distinguish between the different transient species based on the difference between the UV-spectra of CH_3 and CD_3.

(11) Future work

In the previous reports we have presented our work on vinyl and propargyl radicals. We want to continue our investigations of unsaturated radicals including C_2H which may be produced by radiolysis of Ar/C_2H_2 mixtures.
Our preliminary results on COOH/HCOO have been successful in the sence that we have observed an UV-spectrum of the transient species produced by H-abstraction from formic acid. By studies of other source reactions we hope to identify the absorbing species.
Very recently we have obtained our first kinetic results with a new experimental set-up employing pulse radiolysis combined with IR-diodelaser spectrophotometry. High yields of methyl radicals were obtained by pulse radiolysis of 1 mbar CH_3I and the decay of CH_3 was followed by monitoring the transient absorption at the Q(9,9) rotational line of the umbrella mode.
We plan to determine the absolute CH_3 line strength by comparing the maximum of the Q(9,9) absorption with the absorption of NO produced in the reaction $CH_3 + NO_2 \rightarrow CH_3O + NO$. This in situ method should provide a reliable value of the line strength.

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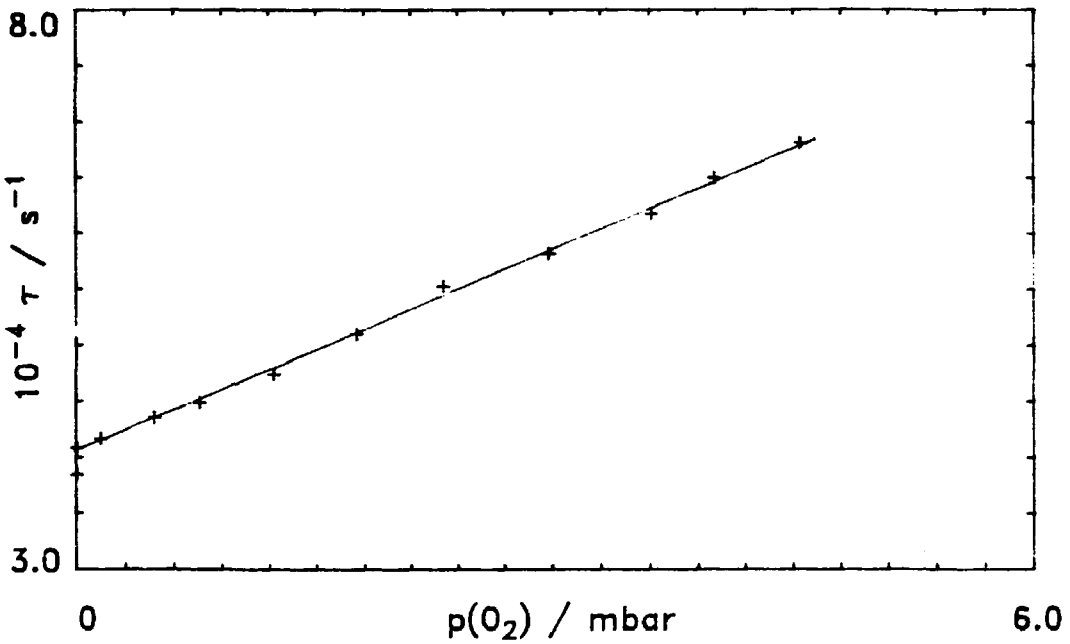
Fig.1 Kinetics of the reaction $C_3H_3 + O_2$



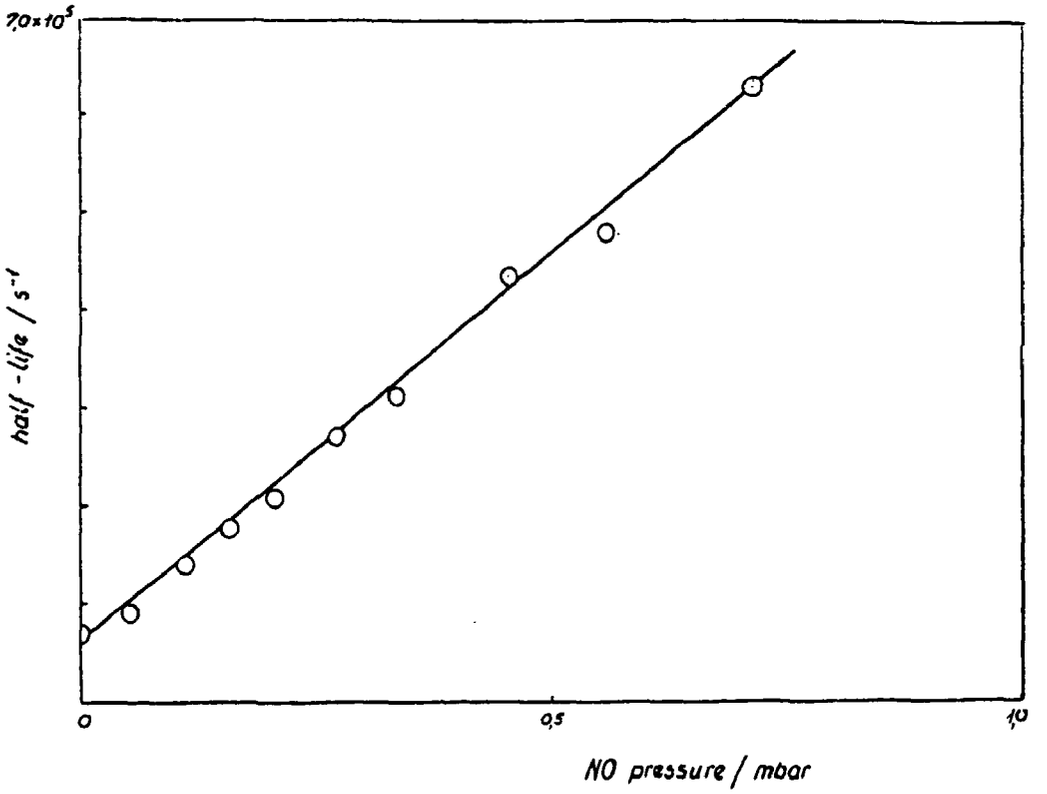
Pulse radiolysis of $Ar/C_3H_3Br/O_2$ mixtures.

$p(C_3H_3Br)$ = 15 mbar. $p(O_2)$ = 0-6 mbar.
$p(Ar)$ = 985 - $p(O_2)$ mbar.
Transient absorption of C_3H_3 monitored at 332 nm.
L = 120 cm. Spectral band pass = 0.2 nm.

Rate constant derived from plot:

$k(C_3H_3 + O_2) = (1.0 \pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$

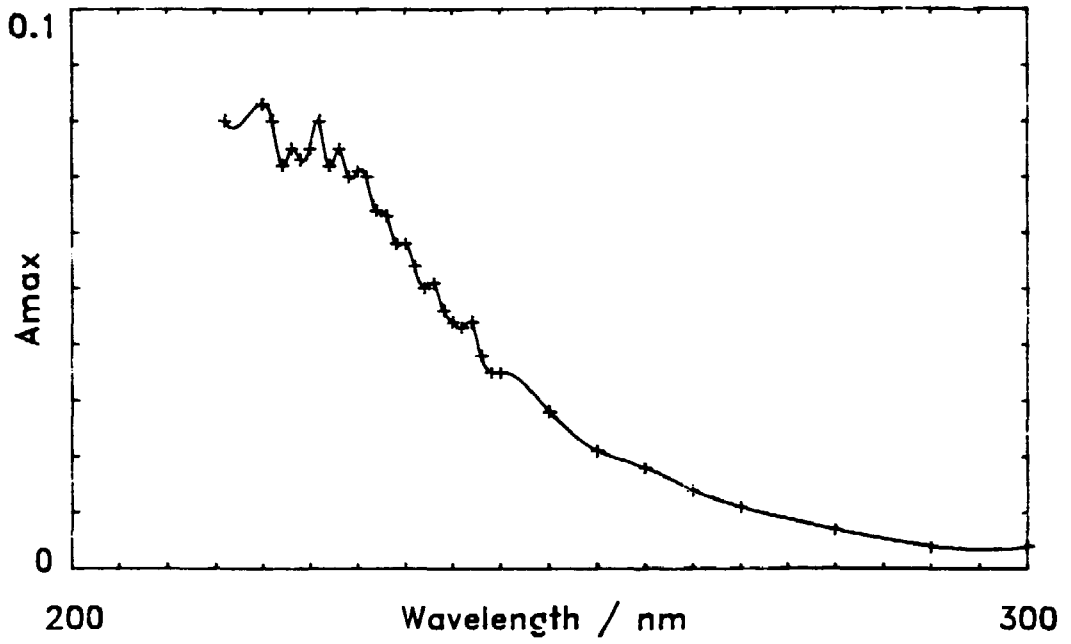
Fig. 2. Kinetics of the reaction NH_2 + NO -> products



Pulse radiolysis of $Ar/SF_6/NH_3/NO$ mixtures

$p(NH_3)$ = 5 mbar. p(NO) = 0-1 mbar. p(Ar) = 995 mbar.
Transient absorption of NH_2 monitored at 597.6 nm.
L = 120 cm; Spectral band pass = 0.1 nm.
Rate constant derived from plot:
$k(NH_2 + NO) = 1.3 \times 10^{10}\ M^{-1}s^{-1}$

Fig.3 Spectrum of COOH and/or HCOO



Transient absorption signals observed by pulse radiolysis of gas mixtures containing 2 mbar HCOOH and 998 mbar SF_6.

Source reaction: F + HCOOH -> HF + COOH/HCOO

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KINETICS AND MECHANISMS OF ELEMENTARY CHEMICAL PROCESSES OF IMPORTANCE IN COMBUSTION

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Abstract (Max. 2000 char.)

The technique of pulse radiolysis combined with transient ultraviolet absorption spectrophotometry has been employed in spectrokinetic studies of shortlived free radical intermediates of importance in combustion. Various source reactions for vinyl, propargyl and carboxyl radicals have been investigated and the UV-spectra of these radicals have been recorded. The spectral features have been utilized in kinetic studies of the self-reactions of the radicals and the reactions with oxygen. Kinetic results on the reaction $NO + NH_2$ are also reported.

Descriptors - INIS

COMBUSTION; NITROGEN OXIDES; PROPARGYL RADICALS; PULSE TECHNIQUES; RADICALS; RADIOLYSIS; SPECTROPHOTOMETRY; ULTRAVIOLET SPECTRA; VINYL RADICALS

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